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(19) (CA) **CANADIAN PATENT** (12)

(54) Treatment of Waste Oils

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Abstract of the Disclosure

Naturally untreatable oils are purified by treatment with calcium hydroxide. The treated oil separates into an oil layer, a water layer and often a sludge layer, which separation may be assisted by centrifugation. The sludge layer is fully limed and is suitable for disposal. The sludge layer may be further dewatered by a freeze-thaw technique.

TREATMENT OF WASTE OILS

The present invention is concerned with the treatment of waste oils.

Many produced crude oils contain impurities which adversely affect refining processes and equipment, and sometimes the properties of the end product. The most common impurities are water, salts and clays and they are usually removed by washing the oil with additional, low mineral-content water. This procedure often results in the production of emulsions, from which the water phase is conventionally separated with the aid of organic chemical de-emulsifiers and electrostatic coalescers. The washing and water separation steps together constitute the process known as "desalting". This process is not sufficient, however, to clean up some crude oils or crude oil fractions, particularly from heavy oil production, and these are often disposed of as waste.

The latter crude oils and fractions are referred to herein as "normally intractible oils" in that they resist the conventional purification procedures. These normally intractible oils contain water and solid impurities, usually clays which are often complexed with organic matter, and their intractible nature is thought to arise from water-in-oil emulsions which are stabilized by the clay solids.

It has now surprisingly been found that the addition of calcium hydroxide to normally intractible oils enables separation of impurities from the oil to occur.

In accordance with the present invention, therefore, there is provided a method of treatment of a normally intractible oil containing water and solids, which comprises treating the oil with calcium hydroxide to cause separation of the intractible oil at least into an oil phase and a water phase.

In the present invention, therefore, a normally intractible oil containing impurities, mainly in the

form water, silts and clays, is treated with calcium hydroxide. The calcium hydroxide treatment may be effected by washing the intractible oil with a solution of calcium hydroxide, preferably a saturated solution, along with additional solid phase calcium hydroxide, if desired, at elevated temperatures, preferably about 60° to about 80°C, in a procedure analogous to conventional crude oil washing with water.

The washing of the intractible oil using the calcium hydroxide solution in accordance with this invention may be effected in any convenient manner. For example, the treatment may be effected during transportation of the intractible oil, for example, by pipeline, tanker or tank truck, or in a stirred reactor constructed for the purpose.

The calcium hydroxide treatment may also be effected by first mixing the intractible oil with a concentrated slurry of solid calcium hydroxide and allowing the mixture to stand at elevated temperature, preferably about 60° to about 80°C, for an extended period of time, usually about 4 to about 24 hours, prior to any further treatment. In this procedure, about 0.2 to about 3 g of $Ca(OH)_2$ per kg may be first mixed with the crude oil or fraction.

Further treatment may then comprise washing with saturated calcium hydroxide solution, as described above, or mechanical dewatering, such as by centrifugation.

The calcium hydroxide treatment surprisingly leads to separation of the intractible oil, substantially complete removal of impurities from the intractible oil and to readily separable oil and aqueous phases.

Any emulsions which form during the washing step are very unstable and usually break without the necessity to use chemical de-emulsifiers. Electrostatic coalescers also are not required, but also may be used to promote more rapid separation of the aqueous phase.

Centrifugation of the calcium hydroxide-treated intractible oil leads to rapid separation into three phases, namely a clear oil phase, an aqueous phase and a clay/asphalt (oil sludge) phase. The pre-treatment with calcium hydroxide is particularly useful in this procedure, since not only does it aid in the destabilization of certain of the emulsions, thereby rendering the centrifugation more efficient, but also leads to a uniformly limed clay/asphalt phase that is more acceptable for road application or landfill, owing to a decreased possibility of trace metal leaching.

The limed sludge is also more amenable to further dewatering by freezing and thawing, which may be effected in western Canada over the winter months in pits, either at the final disposal site or in a temporary location prior to transportation to the final disposal site.

Although other divalent metal compounds are known to destabilize emulsions, calcium hydroxide (or slaked lime) is utilized in this invention because of its low cost and low concentrations precipitate many organic surface active impurities by an acid-base reaction, unlike other alkaline reagents or other calcium compounds, such as calcium chloride. Treatment of many intractible oils by calcium chloride has no effect on the ability to separate the components of the oil.

This invention is illustrated further by the following Examples:

Example 1

This Example illustrates the effect of washing a normally intractible waste oil with saturated calcium hydroxide solution.

A waste oil sample containing absorbed water and various other impurities was mixed vigorously for one minute with an equal volume of saturated calcium hydroxide solution at about 70°C. Excess solid calcium hydroxide was present in the mixture over and above the quantity saturating the calcium hydroxide solution at 70°C (about 500 mg/l). After standing for four hours

at about 70°C, the aqueous phase had separated in volume at least equal to the volume of solution originally added. The presence of an intermediate layer of brown, dispersed material indicated that the upper oil layer had been substantially freed of impurities and the water associated with them.

Example 2

This Example illustrates the effect of adding a concentrated calcium hydroxide slurry to a waste oil in comparison with an equivalent amount of calcium chloride.

Two samples of a normally intractible waste oil from the Swan Hills area of Alberta, Canada, were treated with 250 ppm and 500 ppm of calcium hydroxide and calcium chloride respectively, added as a concentrated suspension or solution in water in the ratio of 1 part of suspension or solution to 50 parts of waste oil. After vigorous mixing and standing at 60°C, the following observations were made:

Time (hrs)	Sample Treatment $Ca(OH)_2$	$CaCl_2$
0	immediate signs of breakout	no sign of breakout
10	lower aqueous phase separated, 9.7% by volume	no separation observed
58	very clear separation of lower aqueous layer, 8.3% by volume	no separation observed

As may be seen from the results presented above, the addition of calcium hydroxide was effective in causing separation of the waste oil while there was no observed effect with the addition of calcium chloride.

Example 3

This Example illustrates the freeze-thaw dewatering of an oil sludge treated with $Ca(OH)_2$.

Approximately 150g of a waste oil sludge obtained from the Brooks area of Alberta, Canada was mixed with 0.9g of hydrated lime at 70°C and then frozen to a temperature of about -10°C. After being maintained

frozen for 19 hours, the material was thawed to room temperature and approximately 50 ml of a water layer was collected. A small amount of a bright oil layer also was observed to form and stick to the sides of the container.

In a parallel experiment, a further sample of the waste oil sludge was frozen and then thawed but without the initial addition of the slaked lime. The separation of a water layer and an oil layer were not observed.

In summary of this disclosure, the present invention provides novel methods for the treatment of normally intractible oils using calcium hydroxide and the recovery of useful products therefrom. Modifications are possible within the scope of this invention.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of treatment of a normally intractible oil containing water and solids, which comprises treating said oil with calcium hydroxide to cause separation of the intractible oil at least into an oil phase and a water phase.

2. The method of claim 1 wherein said intractible oil arises from heavy oil production.

3. The method of claim 1 wherein said calcium hydroxide treatment is effected by washing said intractible oil with an aqueous solution of calcium hydroxide.

4. The method of claim 1, 2 or 3, wherein said calcium hydroxide is used in the form of a saturated solution.

5. The method of claim 1, 2 or 3, wherein said calcium hydroxide is used in the form of a saturated solution, along with additional solid phase calcium hydroxide.

6. The method of claim 1 wherein said intractible oil is mixed with a concentrated slurry of solid calcium hydroxide and the mixture is subjected to centrifugation to effect separation of the intractible oil into said oil phase, said water phase and an oil sludge phase.

7. The method of claim 6 wherein said oil sludge phase is separated and subjected to freeze-thaw dewatering.

8. The method of claim 1 or 6, wherein said calcium hydroxide is used in an amount of about 0.2 to about 3 g of $Ca(OH)_2$ per kg of intractible oil.

9. The method of claim 1 or 6 wherein said calcium hydroxide treatment is carried out at a temperature of about 60° to about 80°C.

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente